The low-frequency density of states for amorphous and crystalline ices

C.A. Tulk[1,2,*], **D.D. Klug**[1], **E.C. Svensson**[1], **V.F. Sears**[1], **J. Katsaras**[1]

[1] Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada
[2] Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

Abstract. Incoherent inelastic neutron scattering studies have been performed on two amorphous polymorphs and two crystalline polymorphs of ice, including high-density amorphous (hda) ice. Subsequent annealing cycles allowed data to be collected from low-density amorphous ice (lda), and crystalline ices Ic and Ih. Data were collected between 5 and 80 K for hda, and between 5 and 120 K for the other phases. The low-frequency ($\nu < 1$ THz) densities of states of the four phases are compared. The data illustrate clearly an excess number of modes in the hda density of states at 5 K centered at 0.65 THz. The magnitude of the excess $g(\nu)$ is considerably reduced upon heating the sample from 5 to 20 K. Above 60 K the density of states of hda was found to exhibit predominantly a Debye behavior, $g(\nu) \propto A\nu^2$, as $\nu \rightarrow 0$ THz. No such excess modes were observed in lda or the two crystalline phases studied.

The low temperature behavior of crystalline and glassy materials of the same composition is known to be strikingly different, particularly as related to the low temperature heat capacity, thermal conductivity and phonon density of states (usually below 3 THz) [1–3]. Above 1 K it is well known that many amorphous, or glassy materials (such as ice [4, 5], amorphous silicon and germanium [6], amorphous SiO_2, SiO_4, As_2S_3) exhibit non-Debye character in their heat capacity, which likely results from an excess phonon density of states in the low frequency region. Recent and more general arguments suggest that the excess modes in glasses may result from phonon scattering arising from density fluctuations on the medium length scale [7], or that the excess modes may be associated with the same motion as the transverse acoustic modes in crystalline silicates [8].

Amorphous phases of ice can be prepared by pressurization of crystalline ice Ih (crystallographically hexagonal) to approximately 12–14 kbar at liquid nitrogen temperature [9].

*Corresponding author. (Fax: +1-630/252-4163, E-mail: ctulk@anl.gov)
Present address: Argonne National Laboratory, 9700 S. Cass Ave. Argonne, IL 60439, USA.

The resulting amorphous phase can be recovered at low temperature (77 K) and one atmosphere and is known as high-density amorphous ice (hda, $\varrho = 1.17$ g·cm^{-3}). Annealing hda at one atmosphere at approximately 115–120 K results in low density amorphous ice (lda, $\varrho = 0.93$ g·cm^{-3}). Further annealing at 160 and 210 K results in a crystallization transformation of the lda phase to cubic ice Ic and hexagonal ice Ih.

The complete phonon density of states of amorphous ice (hda, lda) has been discussed previously [10], as have preliminary neutron scattering experiments on hda aimed at investigating the very low energy transfer region of the phonon density of states [4, 5]. A weighted spectral density of two level states has also been determined from analysis of far IR spectra of hda, lda, and ice Ic/Ih (H_2O and D_2O) studied between 2.7 and 15 K [11].

Subsequent to these studies, Schober [12] has performed similar experiments on D_2O samples of hda, and lda ice at 20 K with no evidence of any excess low frequency modes. However, it is known that the scattering intensity in an energy gain inelastic neutron scattering experiment from deuterium is much weaker than that from hydrogen. Here we report detailed inelastic neutron scattering experiments to study the low frequency region of the phonon density of states of two structurally distinct amorphous ice phases and two crystalline phases of ice as a function of temperature. The results presented here confirm our earlier work [4].

1 Sample production and experimental details

High-density amorphous (hda) ice samples were produced at the National Research Council of Canada by compression of fine-grained polycrystalline ice Ih at liquid nitrogen temperature. A disk shaped sample 69.5 mm in diameter and 2 mm thick was compressed in a cold (77 K) piston-cylinder device placed within a 1000-ton press. After densification the sample was then decompressed, resulting in an amorphous specimen, which was approximately 25% more dense than the ice Ih starting material. The sample was recovered to 1 atmosphere and stored in liquid nitrogen. The recovered

samples were sandwiched between two single crystal silicon wafers and placed in an aluminum sample holder fitted with thermo-couples above and below the sample. The samples were cold loaded (at 77 K) into a large-bore liquid helium cryostat, then cooled to 5 K for initial data collection. The low-density amorphous (lda) ice, cubic ice Ic and ice Ih were produced by successively heating the sample to 115, 155 and 240 K respectively.

The incoherent-inelastic neutron scattering experiments were performed on the N5 triple axes spectrometer in symmetric transmission mode at the NRU reactor at Chalk River. A silicon (111) monochromator and a pyrolytic graphite (002) analyzer were used at a constant momentum transfer of $Q = 2.5\,\text{Å}^{-1}$. Scans were performed with fixed scattered neutron energy, 1.19 THz, and variable incident neutron energy. A sapphire beam filter was placed in the incident beam and a Beryllium beam filter was placed in the scattered beam, both were cooled to approximately 77 K. The energy resolution, the FWHM at the elastic peak, was measured to be 0.05 THz.

To determine the one-phonon velocity spectrum, $f(\nu)$, and thence the one-phonon density of states several corrections were applied to the raw neutron data. These corrections have been described previously [4].

2 Results

Applying the various corrections to the data resulted in very good $g(\nu)$ peak profiles over the entire transverse acoustic mode region and enabled the detailed comparison of the $g(\nu)$ of each amorphous polymorph (along with the two crystalline phases). At higher temperatures, $T = 80$ K, predominantly Debye behavior as $g(\nu) \to 0$ was observed for all four ice phases, see inset in Fig. 2. The TA maximum of hda is located at approximately 2.2 THz, this is shifted to significantly higher frequency than either the lda form, where the TA maximum is at approximately 1.9 THz, or ice Ic/ice Ih where the TA maximum is at approximately 1.8 THz. The higher frequency of the TA maximum in the hda phase is expected considering the approximately 25% increase in density on going from the crystalline phases to hda. The overall features of the lda phase at 80 K are found to be generally similar to the crystalline phases, particularly with respect to the high frequency shoulder found at approximately 2.6 THz for both lda and ice Ic. Note that the densities of ice Ih, ice Ic and lda are similar. On transformation to ice Ih the TA sharpens considerably, most likely due to the annealing of bonding defects created during the rapid hda to lda transformation. The peak width and position relative to the crystalline phases provides conclusive evidence of the successful synthesis of the high-density amorphous ice phase.

Unlike the predominantly Debye character of $g(\nu)$ at 80 K, similar data collected at lower temperatures provide evidence of non-Debye behavior, particularly in the hda phase. Figure 1a illustrates the hda ice density of states collected at $T = 5$ and 80 K. The non-Debye behavior is shown clearly between 0.4 and 0.8 THz, with the largest deviation from $A\nu^2$ behavior occurring at 0.65 THz. The uncertainties in the data are approximately given by the data point size. The gross features, indicating excess modes appear to be unique to the hda phase. Figure 1b shows data collected from lda at 5 and 80 K in the same frequency region after the sample has been heated
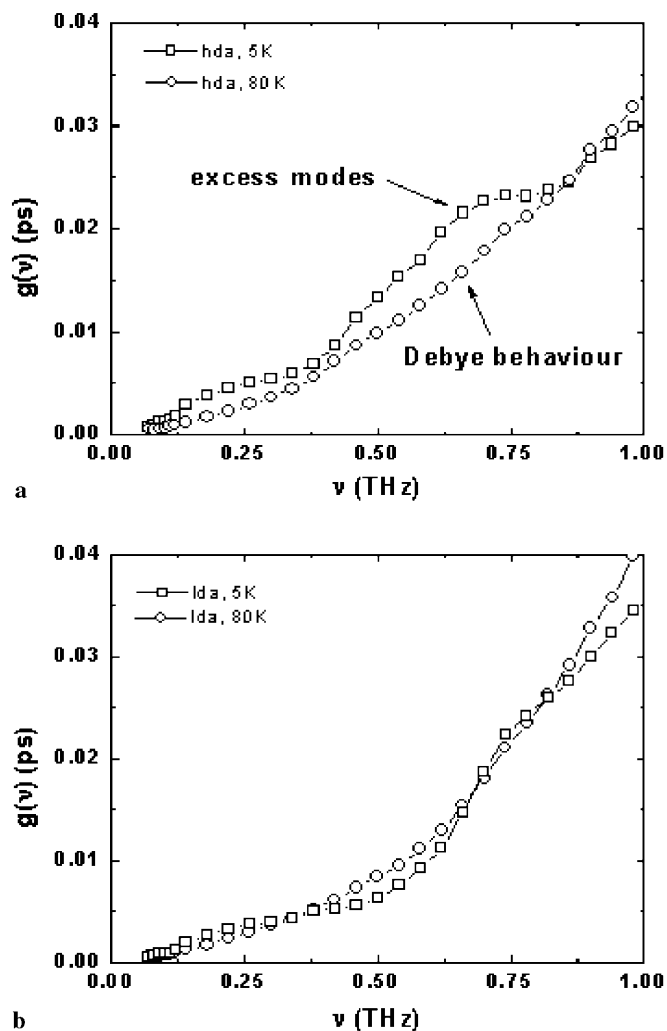

Fig. 1a,b. Comparison of the low frequency density of states of two amorphous phases at $T = 5$ and 80 K
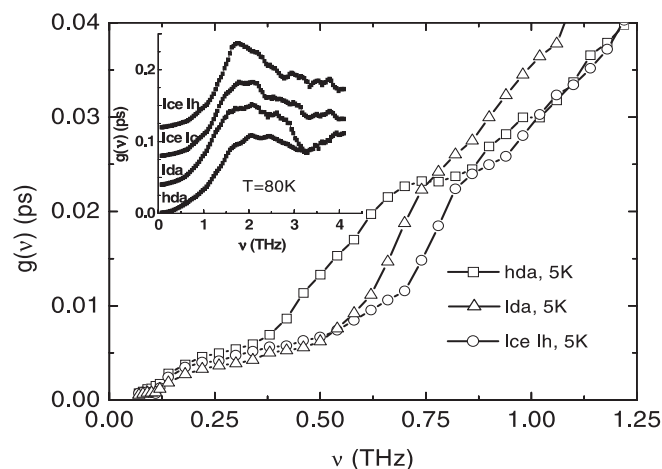

Fig. 2. Comparison of the low frequency density of states of three phases of ice at $T = 5$ K. The inset shows the transverse acoustic mode at $T = 80$ K for each phase studied

to 115 K. Both sets of lda data generally show similar behavior; however, there does seem to be a very subtle deviation from $A\nu^2$ behavior between 0.6 and 0.8 THz in the 5 K data

from the lda phase. The $g(\nu)$ of the lda sample at 5 K drops below the $g(\nu)$ of the sample at 80 K. This kink in $g(\nu)$ at 5 K is only slightly outside the error, in comparison with $g(\nu)$ at 80 K, where the kink seems to be of reduced magnitude, and therefore may not be statistically significant. It is worth noting that the crystalline phases, ice Ih and ice Ic, also exhibit a similar kink and at the moment its origin is not known, and may have several possible origins. It may result from small crystallite size due to the large rapid volume change during the transformation from hda to lda, perhaps resulting in localized modes and/or surface effects [13]. However, this is likely not the case since the sample would have annealed considerably upon heating to 210 K, and the kink is still observed in the ice Ih data. (Note also that the samples were stored at 77 K prior to the experiment.) It is also worth noting that the far-infrared absorptivity of ice Ih has been represented by a sum of two terms [14]. The first term is proportional to the fourth power of the frequency and dominates at high frequency. This is likely caused by the acoustic vibrations made active by orientational disorder. The second term, dominant at lower frequencies, was shown to be proportional to the square of the frequency and is likely caused by the second-order difference bands from the translational optic modes. The cross-over between the two behaviors is thought to occur between 20 and 25 cm^{-1} (0.60 to 0.75 THz). However, the kink in the present data may not be significantly temperature dependent. The non-Debye behavior of the $g(\nu)$ of the hda phase is clearly illustrated when it is compared with both the lda phase and the crystalline phases at low temperature, in Fig. 2. The deviation from both the crystalline ice Ih and lda polymorphs begin at approximately 0.38 THz, with the maximum deviation from the crystalline phase occurring at approximately 0.69 THz.

The temperature dependence of the excess modes in the low frequency region of the density of states of hda has been illustrated between 5 and 80 K in Fig. 3a. There appears to be no significant change in $g(\nu)$ upon increasing the temperature from 60 to 80 K. This is taken as good evidence that the non-Debye character has essentially disappeared at 60 K. It was also noted that while still detectable the excess modes have been reduced considerably on heating the sample from 5 to 20 K, thus these modes are very difficult to distinguish from the underlying Debye character above 20 K. The difference between $g(\nu)$ at 5, 20, 40 and 60 K and $g(\nu)$ at 80 K is plotted in Fig. 3b and nicely illustrates the temperature dependence in this range.

3 Conclusions

Inelastic incoherent neutron scattering has been used to investigate the low frequency phonon density of states, $g(\nu)$, of two amorphous phases (high and low density) and two crystalline phases (ice Ih and ice Ic) of ice. The present results illustrate that excess density of states (above that expected from the Debye $A\nu^2$ behavior) exists in hda ice at 5 K between 0.4 and 0.8 THz with the largest deviation from Debye behavior observed at 0.65 THz. The temperature dependence of the excess intensity resulting from these low frequency modes decreases considerably with increasing temperature and may suggests a two level system. At 80 K all the phases studied show predominantly Debye frequency dependence with little evidence of anomalous behavior.

Finally, the low temperature behavior of $g(\nu)$ of the lda phase seems to be more closely related to the crystalline phases rather than the high-density amorphous phase.
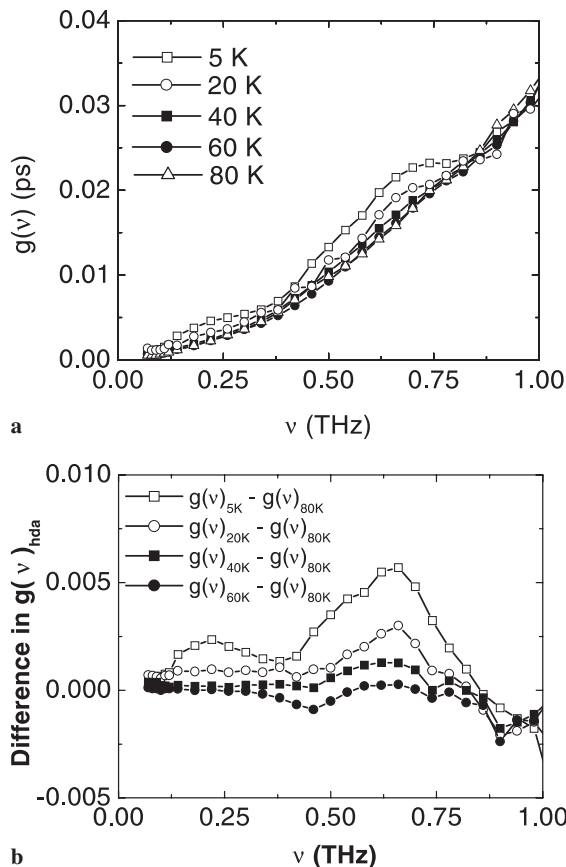
Fig. 3a,b. Temperature dependence of the excess modes in the high-density phase, **a** measured density of states at each temperature, **b** difference at each temperature with respect to that at $T = 80$ K. The errors in **a** are approximated by the symbol size and in **b** are given by the error bar shown

References

1. C. Oligschleger, H.R. Schober: Phys. Rev. B **59**, 811 (1999)
2. H.R. Schober, B.B. Laird: Phys. Rev. B **44**, 6746 (1991)
3. B.B. Laird, H.R. Schober: Phys. Rev. Lett. **66**, 636 (1991)
4. E.C. Svensson, W. Montfrooij, V.F. Sears, D.D. Klug: Physica B **194–196**, 409 (1994)
5. J.S. Tse, D.D. Klug, C.A. Tulk, E.C. Svansson, I. Swainson, V.P. Shpakov, V.R. Belosludov: Phys. Rev. Lett. **85**, 3185 (2000)
6. W.A. Kamitakahara, R. Biswas, A.M. Bouchard, F. Gompf: Physica B **156–157**, 213 (1989)
7. S.R. Elliott: Europhys. Lett. **19**, 201 (1992)
8. M.T. Dove, M.J. Harris, A.C. Hannon, J.M. Parker, I.P. Swainson, M. Gambhir: Phys. Rev. Lett. **78**, 1070 (1997)
9. O. Mishima, L.D. Calvert, E. Whalley: Nature **310**, 3935 (1984)
10. A.I. Kolesnikov, J. Li, S.F. Parker, R.S. Eccleston, C.-K. Loong: Phys. Rev. B **59**, 3569 (1999)
11. N.I. Agladze, A.J. Sievers: Phys. Rev. Lett. **80**, 4209 (1998)
12. H. Schober, M. Koza, A. Tölle, F. Fujara, C.A. Angell, R. Böhmer: Physica B **241–243**, 897 (1998)
13. E. Duval, A. Boukenter, B. Champagnon: Phys. Rev. Lett. **56**, 2052 (1986)
14. O. Mishima, D.D. Klug, E. Whalley: J. Chem. Phys. **78**, 6399 (1983)